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TITLE: Coated optical fiber comprises outer cured coated layer formed from resin composition comprising urethane (meth)acrylate oligomer and (meth)acrylate compound, and has specified modulus of elasticity

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BASIC-ABSTRACT:

NOVELTY - A coated optical fiber comprises outer cured coated layer formed from liquid curable resin composition.

Composition comprises:

(a) urethane (meth)acrylate obtained from reaction of diisocyanate compound, hydroxyl group containing (meth)acrylate compound and/or polyol compound,

(b) (meth)acrylate compound and

(c) polymerization initiator. Cured coating has modulus of elasticity of 50 MPa or more at 23degreesC.

DESCRIPTION - A coated optical fiber comprises an outer cured coating layer formed from a liquid curable resin composition.

The composition comprises:

(a) a urethane (meth)acrylate obtained from reaction of a diisocyanate compound, a hydroxyl group containing (meth)acrylate compound and/or a polyol compound;

(b) a (meth)acrylate compound of formula (I); and

(c) a polymerization initiator. The cured coating has modulus of elasticity of 50 MPa or more at 23degreesC.

$CH_2=C(R_1)-COO-C_nH_{2n+1}$

R1 = H or methyl group; and

n = 4-12

USE - As coated optical fiber.

ADVANTAGE - The cured material has high modulus of elasticity to minimize attenuation loss, favorable breaking elongation to minimize transmission loss and superior surface characteristics with small adhering force to avoid adherence during storage or transportation.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Composition: The composition further comprises a polymerizable unsaturated monomer other than component (b). Preferred Properties: The cured products have modulus of elasticity of 200 MPa or more, breaking elongation of 30% or more and adhering force of 0.08 N/cm or less. The outer coating serves as secondary or bundling material for optical fibers.

Preferred Definition:

n = 8-10

SPECIFIC COMPOUNDS

The component (b) is 2-ethylhexyl acrylate, octyl-decyl acrylate or isodecyl acrylate.

A reactor vessel was charged with polypropylene glycol (402.9 g) having average molecular weight of 3200, tolylene diisocyanate (263.9), 2,6-di-t-butyl-p-cresol (0.24) and phenothiazine (0.08). The mixture was cooled to 15degreesC while stirring. After addition of dibutyl tin dilaurate (0.8), 2-hydroxy propyl acrylate (87.9) was added drop wise. The mixture was stirred and 2-hydroxy ethyl acrylate (244.2) was added drop wise. The reaction was terminated when the residual isocyanate was 0.1 weight percent or less and urethane methacrylate oligomer was obtained. A reactor was charged with polymerizable oligomer (78.2), 2-ethyl hexyl acrylate (10), N-vinylcaprolactam (5), isobornyl acrylate (6.8), Irgacure 651 (1.7), Irgacure 507 (0.4) and Irganox 1035 (0.3). The mixture was stirred at 50degreesC to produce a homogeneous solution of resin composition. The viscosity of the composition was 4.5 Pa.seconds at 25degreesC. The composition was applied on a glass plate, ultraviolet rays were irradiated and modulus of elasticity and breaking elongation of the resulting coated material were determined by JIS K7127 and was found to be 520 MPa and 46%, respectively. The film adherence force of the composition was 0.07 N/cm and the water absorption was 2.3%.

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(54) Title: OPTICAL FIBER COATING COMPOSITIONS

(57) Abstract: A coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition comprising: (A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound, (B) a (meth)acrylate compound shown by the following formula (1), $CH_2=C(R^1)-COO-C_nH_{2n+1}$ wherein R^1 represents a hydrogen atom or a methyl group and n is an integer from 4 to 12, and (C) a polymerization initiator, wherein the cured products of the liquid curable resin composition has a modulus of elasticity of 50 Mpa or more.

OPTICAL FIBER COATING COMPOSITIONS

Field of the Invention

The present invention relates to a liquid curable resin composition capable of producing a cured material having excellent mechanical properties and surface characteristics suitable as an outer coating layer such as a secondary material and bundling material for optical fibers.

Description of related art

In the manufacture of optical fibers, resin coatings are provided over glass fibers prepared by spinning a molten glass for protection and reinforcement. As such a resin coating, a structure consisting of a primary flexible coating layer formed on the surface of optical fibers and a secondary rigid coating layer applied thereon is known. Tape-shaped optical fibers and optical fiber cables comprising a number of fibers provided with these resin coatings bundled using bundling materials are also well known. Resin compositions for primary coating layers are called primary materials, for secondary coating layers are called secondary materials, and for bundling a number of optical fibers are called bundling materials. In addition, a material for further binding several tape-shaped optical fibers and optical fiber cables is also called a bundling material. These resin coatings are usually provided by curing a liquid curable resin composition applied on the surface of the optical fibers by using heat or light, in particular, ultraviolet rays.

Such a secondary material and bundling material must have high modulus of elasticity and excellent mechanical characteristics such as high breaking elongation. Optical fibers, tapes, and cables to which the secondary material or bundling material has been applied are wound around a bobbin, which is stored or transported with the secondary materials or the bundling materials being in contact with each other. For this reason, the secondary materials or the bundling materials must have superior surface characteristics to avoid adherence of these materials.

Accordingly, an object of the present invention is to provide a coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition capable of producing cured products having excellent

mechanical properties and surface characteristics.

Summary of the invention

As a result of extensive studies on liquid curable resin compositions satisfying the both requirements for excellent mechanical properties and surface characteristics, the present inventors have found that a cured material having high modulus of elasticity and breaking elongation, and at the same time, exhibiting superior surface characteristics with a small adhering force can be obtained from a liquid curable resin composition comprising a urethane (meth)acrylate oligomer and a (meth)acrylate compound having an alkyl group containing 4-12 carbons.

Detailed description of the invention

Accordingly, an object of the present invention is to provide a coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition comprising:

(A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound,

(B) a (meth)acrylate compound shown by the following formula (1),

$$CH_2=C(R^1)\text{-}COO\text{-}C_nH_{2n+1} \qquad (1)$$

wherein R^1 represents a hydrogen atom or a methyl group and n is an integer from 4 to 12, and

(C) a polymerization initiator,

wherein the cured products of the liquid curable resin composition have a modulus of elasticity of 50 MPa or more.

The urethane (meth)acrylate of the component (A) which is a polymerizable oligomer can be obtained by reacting a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or by reacting a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound. Specifically, the component (A) can be

obtained by reacting the isocyanate group in the diisocyanate compound with the hydroxyl group in the polyol compound and/or hydroxyl group-containing (meth)acrylate compound.

In the preparation of urethane (meth)acrylate (A-1) from a polyol compound, diisocyanate compound, and hydroxyl group-containing (meth)acrylate, these compounds are preferably used in such proportions that the isocyanate group of the diisocyanate compound and the hydroxyl group of the hydroxyl group-containing (meth)acrylate are respectively 1.1-2 equivalents and 0.1-1 equivalent for 1 equivalent of the hydroxyl group of the polyether polyol. In the preparation of urethane (meth)acrylate (A-2) from a diisocyanate compound and hydroxyl group-containing (meth)acrylate, these compounds are preferably used in such a proportion that the isocyanate group of the diisocyanate compound and the hydroxyl group of the hydroxyl group-containing (meth)acrylate are equivalent.

In addition, it is possible to prepare both the urethane (meth)acrylate (A-1) and the urethane (meth)acrylate (A-2) at the same time by adjusting the amount of a polyol compound, polyisocyanate compound, and hydroxyl group-containing (meth)acrylate compound.

These reactions can be carried out, for instance, by a process of reacting the polyol compound, diisocyanate compound, and hydroxyl group-containing (meth)acrylate compound altogether; a process of reacting the polyol compound and diisocyanate compound, and reacting the resulting compound with the hydroxyl group-containing (meth)acrylate compound; a process of reacting the diisocyanate compound and hydroxyl group-containing (meth)acrylate compound, and reacting the resulting product with the polyol compound; and a process of reacting the diisocyanate compound and hydroxyl group-containing (meth)acrylate compound, reacting the resulting product with the polyol compound, and further reacting the hydroxyl group-containing (meth)acrylate compound.

As a diisocyanate compound which is used for the synthesis of urethane (meth)acrylate (A), an aromatic diisocyanate, alicyclic diisocyanate, aliphatic diisocyanate, and the like can be given. Examples of aromatic diisocyanates include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate,

3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, bis(2-isocyanateethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, tetramethylxylylene diisocyanate, and the like. Examples of alicyclic diisocyanates include isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, 2,5-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and the like. As examples of aliphatic diisocyanates, 1,6-hexane diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, lysine diisocyanate, and the like can be given. Of these, 2,4-tolylene diisocyanate and isophorone diisocyanate are particularly preferred. Aliphatic isocyanates such as IPDI are most preferred. These diisocyanates can be used either individually or in combinations of two or more.

As hydroxyl group-containing (meth)acrylate compounds used in the synthesis of the urethane (meth)acrylate (A), a hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a primary carbon atom (hereinafter designated as "(meth)acrylate containing a primary hydroxyl group") and a hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a secondary carbon atom (hereinafter designated as "(meth)acrylate containing a secondary hydroxyl group") are preferable. A hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a tertiary carbon atom (hereinafter designated as "(meth)acrylate containing a tertiary hydroxyl group") is not preferred because of its inferior reactivity with an isocyanate group.

Examples of the above (meth)acrylate containing a primary hydroxyl group include 2-hydroxyethyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, and (meth)acrylate of the following formula (2):

$$CH_2{=}C(R^2)\text{-}COOCH_2CH_2\text{-}(OCOCH_2CH_2CH_2CH_2CH_2)_m\text{-}OH \qquad (2)$$

wherein R^2 represents a hydrogen atom or a methyl group and m is an integer from 1 to 3.

Examples of the above (meth)acrylate containing a secondary hydroxyl group include 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl

(meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 4-hydroxycyclohexyl (meth)acrylate, compounds obtained by the addition reaction of (meth)acrylic acid and glycidyl group-containing compounds such as alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and the like.

As examples of polyols used for the preparation of the urethane (meth)acrylate (A), polyether diols such as aliphatic polyether diol, alicyclic polyether diol, and aromatic polyether diol, polyester diol, polycarbonate diol, polycaprolactone diol, and the like can be given. These polyols can be used either individually or in combinations of two or more. Polyols with a tri or more valence, which are synthesized by reacting a diol compound and a polyisocyanate, can also be used as the above polyols. There are no specific limitations to a method of polymerizing the structural unit of these polyols. Random polymerization, block polymerization, or graft polymerization can be employed.

As examples of the aliphatic polyether diols, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, polyether diols obtained by ring-opening copolymerization of two or more of ion-polymerizable cyclic compounds, and the like can be given.

As examples of the ion-polymerizable cyclic compounds, cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate can be given.

As examples of the polyether diols obtained by ring-opening copolymerization of two or more of ion-polymerizable cyclic compounds, binary polymers obtained by the ring-opening polymerization of the combinations of monomers such as tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyl tetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, and butene-1-oxide and ethylene oxide, terpolymers obtained by the polymerization of the combinations of monomers such as tetrahydrofuran, butene-1-oxide, and ethylene oxide, and the like can be given.

Moreover, polyether diols obtained by ring-opening

copolymerization of the above ion-polymerizable cyclic compounds and cyclic imines such as ethyleneimine, cyclic lactones such as β-propyolactone and lactideglycolic acid, or dimethylcyclopolysiloxanes can also be used as the above polyether diols.

Examples of commercially available products of the aliphatic polyether diols include PTMG650, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PPG400, PPG1000, EXCENOL720, 1020, 2020 (manufactured by Asahi Oline Co., Ltd.), PEG1000, UNISAFE DC1100, DC1800 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG2000, PPTG1000, PTG400, PTGL2000 (manufactured by Hodogaya Chemical Co., Ltd.), Z-3001-4, Z-3001-5, PBG2000A, PBG2000B, EO/BO4000, EO/BO2000 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), and the like.

As examples of alicyclic polyether diols, alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, alkylene oxide addition diol of 1,4-cyclohexane diol, and the like can be given.

Examples of aromatic polyether diols include alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide addition diol of naphthohydroquinone, alkylene oxide addition diol of anthrahydroquinone, and the like. Commercially available products such as UniolDA400, DA700, DA1000, and DA4000 (manufactured by Nippon Oil and Fats Co., Ltd.) can be used as the aromatic polyether diols.

Examples of polyester diols include polyester diols obtained by reacting a polyhydric alcohol and a polybasic acid, and the like. Examples of the polyhydric alcohol include ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like. As examples of the polybasic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebasic acid, and the like can be given.

As examples of commercially available products of the above polyester diols, Kurapol P-2010, P-1010, L-2010, L-1010, A-2010, A-1010, F-2020, F-1010, PMIPA-2000, PKA-A, PNOA-2010, PNOA-1010 (manufactured by Kuraray Co., Ltd.), and the like can be given.

As examples of the polycarbonate diols, polycarbonate of

polytetrahydrofuran, polycarbonate of 1,6-hexanediol, and the like, and commercially available products such as DN-980, 981, 982, 983 (manufactured by Nippon Polyurethane Industry Co., Ltd.), PC-8000 (manufactured by PPG), and PC-THF-CD (manufactured by BASF) can be given.

As examples of polycaprolactone diols, polycaprolactone diols obtained by reacting □-caprolactone and a diol, and the like can be given. Examples of such diols used for the reaction with ε-caprolactone include ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 1,4-butanediol, and the like. These polycaprolactone diols are commercially available under the trademarks of PLACCEL205, 205AL, 212, 212AL, 220, 220AL (manufactured by Daicel Chemical Industries, Ltd.), and the like.

Examples of polyols other than the above-mentioned polyols include ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentane diol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, dimethylol compound of dicyclopentadiene, tricyclodecanedimethanol, pentacyclodecanedimethanol, □-methyl-□-valerolactone, polybutadiene with a terminal hydroxyl group, hydrogenated polybutadiene with a terminal hydroxyl group, castor oil-modified polyol, polydimethylsiloxane compounds with terminal diols, polydimethylsiloxane carbitol-modified polyol, and the like.

It is possible to use a diamine together with a polyether polyol in the synthesis of the urethane (meth)acrylate (A). Examples of such a diamine include ethylenediamine, tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines containing a heteroatom, polyether diamines, and the like.

Part of the (meth)acrylates containing a hydroxyl group can be replaced by the compounds having a functional group which can be added to an isocyanate group. For example, γ-aminopropyltriethoxysilane, γ-mercaptopropyltrimethoxy-silane, and the like can be used. Use of these compounds improves adhesion to substrates such as glass.

In the synthesis of the urethane (meth)acrylate (A), it is desirable to use a urethanization catalyst, such as copper naphthenate, cobalt naphthenate, zinc naphthenate, dibutyltin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane,

or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane, in the amount from 0.01 to 1 wt% of the total amount of reactants. In addition, such reactions are carried out usually at 5-90°C, and preferably at 10-80°C.

The urethane (meth)acrylate (A) used in the present invention has a polystyrene-reduced molecular weight measured by the gel permeation chromatography in the range of 500-20,000, and preferably 700-15,000. If the molecular weight is less than 500, the cured products may have only a small breaking elongation; if more than 20,000, on the other hand, the resin composition may have unduly high viscosity.

The amount of the urethane (meth)acrylate (A) in the liquid curable resin composition of the present invention is preferably 30-90 wt%, more preferably 55-87 wt%, and particularly preferably 65-85 wt%. If less than 30 wt%, the modulus of elasticity largely depends upon temperatures; if more than 90 wt%, the liquid curable resin composition may have unduly high viscosity.

Given as examples of the component (B) in the liquid curable resin composition of the present invention, which is the (meth)acrylate compound shown by the formula (1), are butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, amyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, iso-octyl (meth)acrylate, nonyl (meth)acrylate, iso-nonyl (meth)acrylate, decyl (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, and lauryl (meth)acrylate. Of these (meth)acrylate compounds, the compounds having an integer 8, 9 or 10 for n in the formula (1) are preferred in view of processability. Most preferred are n=8 or 9. A particularly preferred (meth)acrylate compound in view of low viscosity is 2-ethylhexyl acrylate having an integer 8 for n in the formula (1), and isodecylacrylate, having an integer 10 for n; another preferred compound is octyldecylacrylate.

The proportion of the (meth)acrylate compound (B) in the liquid curable resin composition of the present invention is preferably 1-60 wt%, and more preferably 3-30 wt%. If less than 1 wt%, the effect of improvement in the mechanical properties and surface characteristics is insufficient; if more than 60 wt%, volatility of the resin composition is unacceptably high.

As the polymerization initiators (C) in the liquid curable resin composition of the present invention, either a heat polymerization initiator or a photopolymerization initiator can be used; photopolymerisation is strongly

preferred because of cure speed.

If the liquid curable resin composition of the present invention is cured by heat, a heat polymerization initiator such as a peroxide or azo compound can usually be used. Specific examples include benzoyl peroxide, t-butyloxy benzoate, azobisisobutyronitrile, and the like.

If the liquid curable resin composition of the present invention is cured by irradiation of lights, a photopolymerization initiator is used. Optionally, a photosensitizer can also be added. Given as examples of the photopolymerization initiator are 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diamino-benzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2- methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2- isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; IRGACURE 184, 369, 651, 500, 907, CGI 1700, CGI 1750, CGI 1850, CG24-61, Darocur 1116, 1173 (manufactured by Ciba Specialty Chemicals Co.); Lucirin LR8728 (manufactured by BASF); and Ubecryl P36 (manufactured by UCB). Examples of photosensitizers include triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, 4-methyl dimethylaminobenzoate, 4-ethyl dimethylaminobenzoate, 4-isoamyl dimethylaminobenzoate; Ubecryl P102, 103, 104, 105 (manufactured by UCB); and the like.

The proportion of the polymerization initiator (C) used in the liquid curable composition of the present invention is preferably 0.1-10 wt%, and more preferably 0.3-7 wt%.

In addition to the above components, a polymerizable unsaturated monomer (D) other than the (meth)acrylate compound (B) may be added to increase curability and adjust the viscosity of the liquid curable resin composition of the present invention in the amount of 0-60 wt%, and preferably 3-40 wt%. If more than 60 wt% of the component (D) is added, temperature dependency of the modulus of elasticity of the cured products may increase.

Mono-functional compounds and poly-functional compounds are given as examples of the polymerizable unsaturated monomer (D). Given as

examples of monofunctional compounds are vinyl group-containing lactam such as N-vinylpyrrolidone and N-vinylcaprolactam, alicyclic structure-containing (meth)acrylates such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloylmorpholine, vinylimidazole, vinylpyridine, and the like. In addition to the above compounds, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl acrylate, stearyl (meth)acrylate, iso-stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylamino propyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether, and the like can be given.

As examples of commercially available products of the monofunctional compound used as the polymerizable unsaturated monomer, ARONIX M-111, M-113, M-114, M-117 (manufactured by Toagosei Co., Ltd.), KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku Co., Ltd.), IBXA, Viscoat3700 (manufactured by Osaka Organic Chemical Industry, Ltd.), and the like can be given.

Examples of polyfunctional compounds include trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxyethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth)acrylate of diol of ethylene oxide or propylene oxide adduct of bisphenol A, di(meth)acrylate of diol of ethylene oxide or propylene oxide adduct of hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, triethylene glycol divinyl ether, and the like. Examples of commercially available products of the above polyfunctional compounds include

Yupimer UV SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.), Viscoat 700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD R-604, DPCA-20, DPCA-30, DPCA-60, DPCA-120, HX-620, D-310, D-330 (manufactured by Nippon Kayaku Co., Ltd.), ARONIX M-210, M-215, M-315, M-325 (manufactured by Toagosei Co., Ltd.), and the like.

Various additives such as antioxidants, coloring agents, UV absorbers, light stabilizers, silane coupling agents, heat polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, wettability improvers, and coating surface improvers can also be added in addition to the above components, as required. As examples of the antioxidants, Irganox 1010, 1035, 1076, 1222 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Antigene P, 3C, FR, GA-80, (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like can be given. As examples of the UV absorbers, Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Seesorb 102, 103, 110, 501, 202, 712, 704 (manufactured by Shipro Kasei K.K.), and the like can be given. As examples of the light stabilizers, Tinuvin 292, 144, 622LD (manufactured by Ciba Specialty Chemicals Co., Ltd.), Sanol LS770 (manufactured by Sankyo Co., Ltd.), TM-061 (manufactured by Sumitomo Chemical Co., Ltd.), and the like can be given. As examples of the silane coupling agents, γ-aminopropyltriethoxysilane, γ-mercaptopropyltrimethoxy-silane, γ-methacryloxypropyltrimethoxysilane, and the like, and commercially available products such as SH6062, 6030 (manufactured by Dow Corning Toray Silicone Co., Ltd.), and KBE903, 603, 403 (manufactured by Shin-Etsu Chemical Co., Ltd.) can be given.

Furthermore, other oligomers and polymers, as well as other additives can optionally be added to the liquid curable resin composition of the present invention inasmuch as characteristics of the composition of the present invention are not impaired.

Examples of such other oligomers and polymers include polyester (meth)acrylate, epoxy (meth)acrylate, polyamide (meth)acrylate, siloxane polymers having a (meth)acryloyloxy group, glycidyl methacrylate, and the like.

The composition of the present invention is cured by heat or radiation. Radiation used herein includes infrared rays, visible rays, ultraviolet rays, X-rays, electron beams, α-rays, β-rays, γ-rays, and the like. Particularly preferred radiation is ultraviolet rays.

In view of ensuring excellent handling properties and applicability, the viscosity of the liquid curable resin composition of the present invention is in the range of 0.1-10 Pa·s, preferably 1-8 Pa·s, and particular preferably 2-6 Pa·s.

Cured materials made from the resin composition of the present invention have high modulus of elasticity and breaking elongation, and at the same time, exhibit superior surface characteristics with a small adhering force. Therefore, the resin composition is useful as a secondary material or bundling material for optical fibers. The cured material must have modulus of elasticity of at least 50 MPa, preferably more than 200 MPa, and particularly preferably more than 400 MPa. If the modulus of elasticity is less than 50 MPa, an attenuation loss of the optical fiber may be too large to serve the product to the above-mentioned application. In addition, the cured product preferably has breaking elongation of 20% or more, preferably 25% or more, and more preferably 30% or more. If the breaking elongation is less than 20%, optical fibers may be more easily broken. Moreover, the cured products preferably have a water absorption rate of 3% or less, preferably 2.7% or less, and more preferably 2.4% or less. If the water absorption rate is more than 3%, the transmission loss may increase when the optical fiber is dipped in warm water.

A film adhering force is a particularly important characteristic because optical fibers are stored or transported under the conditions in which secondary materials or bundling materials are in contact with each other. For this reason, film adhering force preferably is 0.09 N/cm or less, preferably 0.08 N/cm or less, and more preferably 0.07 N/cm or less.

The present invention will be explained in more detail by examples, which are not intended to be limiting of the present invention.

Preparation Example 1

Synthesis example of urethane (meth)acrylate

A reaction vessel equipped with a stirrer was charged with polypropylene glycol having a number average molecular weight of 3200 (402.9 g), tolylene diisocyanate (263.9 g,) 2,6-di-t-butyl-p-cresol (0.24 g), and phenothiazine (0.08 g). The mixture was cooled to 15°C while stirring. After the addition of dibutyl tin dilaurate (0.8 g), 2-hydroxypropyl acrylate (87.9 g) was added dropwise while controlling the temperature to less than 30°C. After the addition, the mixture was stirred for one hour at 40°C. Next, 2-hydroxyethyl acrylate (244.2 g) was added dropwise while controlling the temperature to less than 60°C. After the addition, the mixture was stirred at 60°C. The reaction was terminated when the residual isocyanate was 0.1 wt% or less. The urethane (meth)acrylate oligomer thus obtained is designated as "Polymerizable oligomer (a)".

Examples 1-2 and Comparative Example A-B

A reaction vessel equipped with a stirrer was charged with the compounds listed in Table 1 in the proportion shown in Table 1. The mixture was stirred at 50°C to produce a homogeneous solution, thus obtaining the compositions of Examples and Comparative Examples. Mechanical properties, viscosity, and surface characteristic of the resulting cured products were evaluated according to the following methods. Results are shown in Table 1.

(1) Measuring method of viscosity

The viscosity at 25°C of the compositions obtained in Examples and Comparative Examples was measured. Viscometer B8H-BII manufactured by Tokimeck Co., Ltd. was used for the viscosity measurement.

(2) Measuring methods of modulus of elasticity and breaking elongation

Modulus of elasticity and breaking elongation of the cured products obtained from the compositions of Examples and Comparative Examples were measured. The liquid compositions were applied to a glass plate using an applicator with a thickness of 381 μm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm^2 in air to form cured coatings having a thickness of about 200 μm. Test specimens for measurement of modulus of elasticity and breaking

elongation were obtained by cutting the cured films into strips with a width of 0.6 cm. The modulus of elasticity and breaking elongation were measured according to JIS K7127 using the test specimens thus obtained. The measurement was carried out at a bench mark distance of 25 mm, a temperature of 23°C, and a humidity of 50%RH. Drawing rates of 1 mm/min and 50 mm/min were adopted respectively for measurement of modulus of elasticity and breaking elongation.

(3) Evaluation method for surface characteristics

An adhering force between cured films obtained in Examples and Comparative Examples were measured to evaluate the surface characteristics. The liquid compositions were applied to a glass plate using an applicator with a thickness of 127 μm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm^2 in air to form cured coatings having a thickness of about 70 μm. The cured film was divided into two pieces, which were immediately caused to adhere with the upper surfaces (the surfaces which had been in contact with air) face-to-face. The adhered films were conditioned at 23°C and 50% RH for 24 hours, and cut into strips with a width of 1 cm to obtain test specimens for measuring adhering force. The adhered films were held with upper and lower chucks of a tensile machine and peeled at a tensile rate of 50 mm/min. to measure the force required for the films to be peeled. The measurement was carried out at a temperature of 23°C and a relative humidity of 50%. The smaller the adhesion force, the better the surface characteristics.

(4) Measuring method of water absorption

The water absorption rate of the cured materials made from the compositions obtained in Examples and Comparative Examples was measured. The liquid compositions were applied to a glass plate using an applicator with a thickness of 381 μm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm^2 in air to form cured coatings having a thickness of about 200 μm. The cured film was cut into pieces having a weight of about 1 g each and dried at 50°C under reduced pressure for 24 hours, before measuring the weight (W1). Next, the cured film pieces were dipped in water at 23°C for 24 hours, followed by measurement of the weight (W2). The cured film pieces were dried at 50°C under reduced pressure for 24 hours, then the weight (W3) was measured. The water absorption

rate was determined according to the following formula (1).
Water absorption (%) = 100 x (W2 - W3)/W1

The components shown in Table 1 are as follows.
Irgacure 651 and Irgacure 907: Photopolymerization initiator (manufactured by Ciba Specialty Chemicals Co.)
Irganox 1035: Antioxidant (manufactured by Ciba Specialty Chemicals Co.)

[Table 1]

	Example		Comparative Example	
	1	2	A	B
Component				
Polymerizable oligomer (a)	78.2	78.2	78.2	78.2
2-Ethylhexyl acrylate	10	15	-	-
N-vinylcaprolactam	5.0	5.0	5.0	5.0
Isobornyl acrylate	6.8	1.8	16.8	1.8
Trimethylolpropane triacrylate	-	-	-	15
Irgacure 651	1.7	1.7	1.7	1.7
Irgacure 907	0.4	0.4	0.4	0.4
Irganox 1035	0.3	0.3	0.3	0.3
Total	102.4	102.4	102.4	102.4
Evaluation items				
Viscosity (Pa·s)	4.5	3.3	8.5	15
Modulus of elasticity (MPa)	520	460	750	970
Breaking elongation (%)	46	36	40	23
Film adhering force (N/cm)	0.07	0.06	0.14	0.10
Water absorption (%)	2.3	2.2	2.3	2.5

As can be seen from Table 1, the liquid curable resin compositions comprising a urethane (meth)acrylate oligomer (A), C_4-C_{12} alkyl (meth)acrylate (B), and polymerization initiator exhibit excellent bundling properties and produce cured products having not only high modulus of elasticity and breaking elongation, but also superior surface characteristics with small adhering force.

CLAIMS

1. Coated optical fiber comprising an outer coating layer being a cured coating from a liquid curable resin composition comprising:
(A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound,
(B) a (meth)acrylate compound shown by the following formula (1),

$$CH_2{=}C(R^1)\text{-}COO\text{-}C_nH_{2n+1} \qquad (1)$$

wherein R^1 represents a hydrogen atom or a methyl group and n is an integer from 4 to 12, and
(C) a polymerization initiator,
wherein the cured coating of the liquid curable resin composition has a modulus of elasticity of 50 MPa or more at 23^0C.
2. The coated optical fiber according to claim 1, wherein the integer n in the formula (1) is 8, 9 or 10.
3. The coated optical fiber according to claim 2, wherein the component (B) is 2-ethylhexyl acrylate, octyl-decylacrylate or isodecylacrylate.
4. The coated optical fiber according to any one of claims 1-3, further comprising a component (D) which is a polymerizable unsaturated monomer other than the component (B).
5. The coated optical fiber according to any one of claims 1 to 4, of which the cured products have modulus of elasticity of 200 MPa or more.
6. A coated optical fiber according to any one of claims 1 to 5, in which the cured coating has a breaking elongation of 30% or more.
7. A coated optical fiber according to any one of claims 1 to 6, in which the cured coating has an adhering force of 0.08 N/cm or less.
8. A coated optical fiber according to any one of claims 1 to 7 wherein the outer coating is a secondary material or a bundling material for optical fibers.

INTERNATIONAL SEARCH REPORT

Inte .ional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C25/10 C09D175/16 C08F283/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C09D C08G C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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